On the Relation among γ-, η- and δ-Al_2O_3 under Hydrothermal Condition

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What was formerly called simply γ-Al_2O_3 may in truth consist of the three forms of γ-, η- and δ-Al_2O_3. The γ-Al_2O_3 is usually obtained by dehydration of good crystalline boehmite γ-$Al_2O_3 \cdot H_2O$ in air over 500°C[1]. The crystal structure is considered to be closely related to that of spinel $MgO \cdot Al_2O_3$[2,3] with a small amount of strongly bound water[4,5], but slightly deformed tetragonally with a lattice constant $a=b=7.96$ and $c=7.82$ Å[6,7]; the (400) peak in the spinel indice in the X-ray diffraction diagram is slightly split into a doublet. The η-Al_2O_3 has been proposed[8] as a product of the dehydration of bayerite α-$Al_2O_3 \cdot 3H_2O$. Its X-ray diffraction diagram seems extremely similar to that of γ-Al_2O_3 except for the (400) peak being hardly split at all[9]. The δ-Al_2O_3 has been proposed as a product of the further heating of γ-Al_2O_3[10]; the peaks in the X-ray diffraction diagram are somewhat sharp and have, except for the weak ones, mostly been attributed to the spinel indice. The existence of η- and of δ-Al_2O_3 as discrete forms independent of γ-Al_2O_3 has been doubted[11]. The present authors have therefore investigated the relation among γ-, η- and δ-Al_2O_3 under hydrothermal conditions.

The starting material was obtained by the dehydration of good crystalline boehmite at 700°C in air. The X-ray diffraction diagram is that of γ-Al_2O_3. This was treated hydrothermally under 20 to 100 atm. at 450 to 500°C. One of the X-ray diffraction diagrams of the products is shown in Fig. 1. There can easily be noticed a remarkable split about the peak (400) in the spinel indice. The diagram about the (400) peak was examined by slow-scanning X-ray diffraction (Geigerflex, Ni filtered Cu$K\alpha$ 30 kV. 10 mamp. irradiation; 1° 1° 0.2 mm. slit system; rate meter, 16; time constant, 4 sec.; scanning speed, 1°/2 min.). The results of the products under various hydrothermal conditions are as shown in Fig. 2 and as summarized in Table I. Under such condition, γ-Al_2O_3 was more deformed tetragonally. The degree of deformation increased as

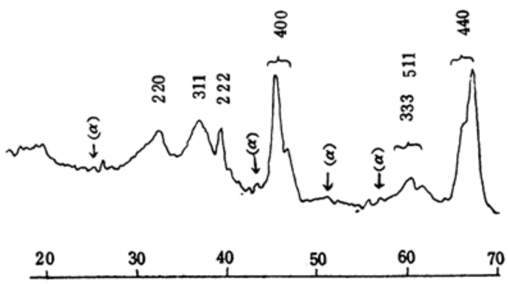

Fig. 1. (γ-Al_2O_3 treated under 50 atm. at 500°C for 15 hr.) No. 9 (α) indicates α-Al_2O_3.

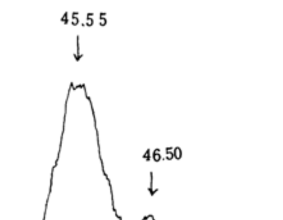

Fig. 2. (400) peak of (γ-Al_2O_3 treated under 100 atm. at 450°C for 13 hr.) No. 7.

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TABLE I. TETRAGONAL DEFORMATION OF γ-Al_2O_3 UNDER HYDROTHERMAL CONDITION

Specimen No.	Treatment	2θ and d spacing, Å (400) and (040)	(004)	Lattice constant, Å $a=b=$	$c=$	a/c	Remark
1	Starting	45.72	(46.38)				
	Material	1.983	(1.956)	7.93	(7.82)	(1.014)	
2	after B. C.						
	Lippens[7]			7.96	7.82	1.018	
3	450°C 20 atm.	45.62	46.44				
	15 hr.	1.987	1.954	7.95	7.81	1.018	
4	450°C 20 atm.	45.51	(46.52)				
	20 hr.	1.992	(1.951)	7.97	(7.80)	(1.022)	
5	450°C 50 atm.	45.58	(46.45)				
	17 hr.	1.989	(1.953)	7.95	(7.81)	(1.018)	
6	450°C 50 atm.	45.40	(46.55)				
	45 hr.	1.996	(1.949)	7.98	(7.80)	(1.023)	
7	450°C 100 atm.	45.44	46.50				
	13 hr.	1.990	1.951	7.96	7.81	1.019	
8	450°C 100 atm.	45.32	46.58				
	18 hr.	2.000	1.948	8.00	7.79	1.027	
9	500°C 50 atm.	45.21	46.79				Fig. 1. Small
	15 hr.	2.004	1.940	8.02	7.76	1.033	amount of α-Al_2O_3 included

TABLE II. TETRAGONAL DEFORMATION DECREASE DUE TO RE-HEATING IN AIR

Specimen No.	Treatment	2θ and d spacing, Å (400) and (040)	(004)	Lattice constant, Å $a=b=$	$c=$	a/c	Remark
3′	Heated No. 3	45.58	46.33				cf. No. 3.
	at 800°C	1.989	1.958	7.95	7.83	1.015	ig. loss 3.3%
6′	Heated No. 6	45.46	46.33				
	at 800°C	1.993	1.958	7.97	7.83	1.018	cf. No. 6.
9′	Heated No. 9	45.40	46.46				Fig. 2
	at 800°C	1.996	1.953	7.98	7.81	1.022	ig. loss 7.6% cf. No. 9

the hydrothermal pressure became high and as the reaction period lengthened. Corundum α-Al_2O_3 was directly obtained from γ-Al_2O_3, while good crystalline γ-Al_2O_3 or δ-Al_2O_3 was not found in the present work.

The tetragonally-deformed γ-Al_2O_3 were re-heated in air at 800°C. The results are summarized in Table II. The degree of tetragonal deformation decreased with re-heating.

The present authors were able to prepare γ-Al_2O_3 with various degrees of tetragonal deformation. The lattice constant could not be determined precisely, for it varied with the conditions of formation. This led us to conclude that there may be η-Al_2O_3 as an extrapolated form of γ-Al_2O_3 with little tetragonal deformation. Good crystalline γ-Al_2O_3 or δ-Al_2O_3 was not found under the hydrothermal conditions.

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